

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Calcium and Magnesium Carbonates

We, LICENCIA TALÁLMÁNYOKAT ERTÉKESÍTŐ VÁLLALAT, a Body Corporate duly organized under the laws of Hungary of 10 József nádor ter, Budapest V, Hungary, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for reacting carbon dioxide with solutions or suspensions of hydroxides under pressure.

According to the present invention there is provided a process for the production of substantially pure powdered calcium carbonate and/or a solution of magnesium bicarbonate from a natural mineral containing calcium or magnesium carbonate, or both, which comprises calcining the natural mineral to convert its carbon to oxide, slaking the oxide(s) with water to give hydroxide(s) reacting the resulting suspension of the hydroxide(s) with carbon dioxide in a reactor in which said hydroxide suspension and gases comprising carbon dioxide are introduced at substantially the same pressure and are forced to flow continuously upwardly under pressure against gravity, and thereafter recovering the powdered calcium carbonate and/or solution of magnesium bicarbonate.

The invention is based on the recognition that if carbon dioxide and suspensions containing calcium and/or magnesium hydroxides are fed into a reaction at equal pressure and then passed together upwardly against gravity in the reactor the desired carbonation reaction between the carbon dioxide and the hydroxide suspension or solution can be continuously,

quickly and quantitatively carried out. It is furthermore possible to keep the reaction parameters between the desired limits, and also to increase the speed of the reaction by using vibrational energy.

The reactants, viz the hydroxide solution or suspension and the carbon dioxide are passed into the reactor at substantially equal pressure and thus flow up through the reactor together.

The carbonation reaction between the carbon dioxide and the hydroxide solution or suspension is preferably carried out under vibration e.g. employing an ultrasonic generator.

The carbon dioxide is preferably introduced into the reaction through a porous or perforated surface in order to distribute the carbon dioxide in the solution or suspension in the form of fine bubbles.

Ultrasonic energy has the effect of reducing the particle size of calcium carbonate produced and furthermore by varying the ultrasonic frequency the crystal form of the calcium carbonate obtained can be varied.

When the process according to the invention is used for treating minerals containing both calcium carbonate and magnesium carbonate, e.g. for treating dolomite, a slurry containing dissolved magnesium bicarbonate and precipitated calcium carbonate is formed, from which the precipitated calcium carbonate can be recovered by filtering under pressure and drying.

Decomposition of an aqueous solution of magnesium bicarbonate occurs under atmospheric pressure at temperatures above about 45° C, and accordingly when carrying out the reaction at this temperature it is preferred

to use a small excess pressure, e.g. 2 to 4 atmospheres gauge pressure, and above this temperature to use higher pressures e.g. 6 to 10 atmospheres gauge pressure.

5 Since the magnesium bicarbonate obtained has a high degree of purity it is useful for preparing magnesium oxide which can be employed e.g., in preparing magnesium metal by chlorination and by electrolysis of the mag-
10 nesium chloride so obtained. Pure carbon dioxide is obtained as a useful by-product of this process.

For any given batch of starting materials employed in the process of the present invention it may be necessary to effect minor variations in the reaction conditions employed in order to obtain the optimum yield of pure product. Accordingly trial runs should be effected to determine the precise conditions of temperature, pressure, concentration and flow rate through the reactor.

Waste gases obtained from the calcination of the mineral can of course usefully be used to provide the carbon dioxide.

25 The process according to the invention is preferably carried out using a reactor comprising a tubular reaction space, the longitudinal axis of the said reaction space being arranged in a position deviating not more than 15° from the perpendicular, the average cross-section of the said reaction space amount-
30 ing to not more than 1200 cm², and the ratio of the length and the average diameter of the said reaction space being at least 15.

35 The reactor must have a carbon dioxide inlet and a hydroxide suspension inlet, said inlets being arranged at the lower end of the reactor. A gas-distributing space is preferably situated adjacent said gas inlet and a space serving to separate the gases and the solutions or suspensions is situated at the upper end of the reactor.

40 The reactor is preferably fitted with a vibrator preferably an ultrasonic vibrator fitted below the reactant inlets and preferably situated symmetrically with respect to the longitudinal axis of the reactor.

45 The cross-section of the reactor may be of any form, but is preferably circular or polygonal.

50 Such a rotor useful for carrying out the process according to the invention will now be described with reference to the accompanying drawing.

55 Referring to the drawing, in operation of the reactor, the hydroxide suspension is fed through a tap 2 by the aid of a pump into the reaction space 1 of the reactor, and a gas comprising carbon dioxide is passed into the gas-distributing space 5 via a gas inlet valve 3. In the gas-distributing space 5 a porous ceramic cylinder 4 is arranged, which distributes the gas in the solution or suspension in the form of fine bubbles. At the

lower end of the reactor a vibrator 6 may be attached. 65

The gas and the hydroxide suspension pass from the reaction space 1 into the closed vessel 7 in which the carbon dioxide and the solution or suspension are separated, whereafter the carbon dioxide leaves the space 7 through the throttle valve 9 and the solution or suspension is led away through the valve 8. 70

No pump for feeding in the solution or suspension is needed if the liquid or suspension is fed into the lower part of the reactor from a container the height of which ensures a hydrostatic pressure equal to the feed pressure necessary. The closed separating space 7 may be opened, and thereby the valve 9 may be omitted if the carbon dioxide leaving the reaction space 1 is not required. 80

The by-product waste materials remaining after the purification of the aqueous slurry obtained by hydrating calcined dolomite can be used in the building industry for producing wall panels and other building elements. 85

The process according to the invention will now be illustrated with reference to the following Examples. 90

EXAMPLE 1

100 kg. of ground dolomite was calcined at a temperature of from 1050 to 1200° C, and the material thus obtained slaked in an open vessel with 400 litres of tap water at 70 to 85° C. The resulting suspension was stirred for one hour and then diluted with a further 400 litres of tap water. The diluted suspension was purified from the unhydrated particles and other impurities using a hydrocyclone having a diameter of 70 mm. The purified suspension was then further diluted to a concentration of 3 to 5% by weight solids, and passed at a rate of 4.4 cm./sec. through a tubular reactor 5 metres long and having an average cross-sectional area of 110 cm², at a pressure of 3 to 4 atmospheres gauge pressure where it was reacted with 7 to 9 volumes of pure carbon dioxide at 3 to 4 atmospheres gauge pressure per volume of suspension. The resulting suspension was filtered. The precipitated calcium carbonate remaining on the filter was dried to give 52 kg. of a fine-grained calcium carbonate having a purity of 98.5% by weight. 95

100 The filtrate was warmed up to a temperature of from 85 to 90° C, whereby all the magnesium hydrogen carbonate in solution in the filtrate was converted to magnesium carbonate. After filtering and drying, 43 kg. of magnesium carbonate were obtained from which, after calcining, magnesium oxide having a purity of 99.2% by weight was obtained. The filter water could be used in a further slaking operation. 105

EXAMPLE 2

The general procedure of Example 1 was 120 125

repeated except that the slaking operation was effected in a closed autoclave at 2 to 3 atmosphere gauge pressure, instead of in an open vessel, the slaking time being thereby reduced to 15 to 20 minutes.

EXAMPLE 3

The general procedure of Example 1 was repeated except that during the slaking of the suspension of the hydroxides, the suspension was subjected to ultrasonic energy having a frequency of 0.8 mega-cycles per second and an intensity of 10–20 watt/cm²; the vibrator was centrally located under the slaking vessel. The slaking time was thereby reduced to 15 minutes and the fineness of the suspension was increased to such an extent that, after reaction with the carbon dioxide, the precipitated calcium carbonate had a grain size not exceeding 1 μ .

EXAMPLE 4

The general procedure of Example 1 to 3 was repeated except that during the introduction of the carbon dioxide into the reactor, the suspension containing calcium hydroxide and magnesium hydroxide was subjected to ultrasonic energy having a frequency of 0.8 mega-cycles per second and an intensity of 10–20 watt/cm². The vibrator was located in the centre of the lower end of the tubular reactor. The reaction rate with the carbon dioxide was thereby accelerated and the degree of fineness of the calcium carbonate precipitate obtained was also increased.

When ultrasonic energy was also employed during the slaking operation, the grain size of the precipitated calcium carbonate is further decreased to not greater than 0.9 μ .

EXAMPLE 5

100 kg. of limestone were calcined at a temperature of 1200° C. and the calcium oxide obtained was slaked with 450 litres of tap water at a temperature of 50° C. The calcium hydroxide obtained was separated from unhydrated particles and other impurities using a hydrocyclone having a diameter of 70 mm. The purified suspension was then diluted with tap water to 1000 litres to give a 5% suspension and the suspension was passed at a rate of 8 litres per minute through a tubular reactor 8 metres long and having an average cross-sectional area of 200 cm² at a pressure of 5 atmospheres gauge pressure wherein it was reacted with 45 to 33 volumes of a purified waste gas containing 30 to 35% by volume of carbon dioxide per volume of suspension. The resulting calcium carbonate precipitate was filtered off, dried, and then loosened on a sieve. 87.6 kg. of precipitated calcium carbonate having a purity of 98.7% by weight and an apparent density of 280 g/litre were obtained.

EXAMPLE 6

The general procedure of Example 5 was repeated except that during the reaction with carbon dioxide the reaction medium was subjected to ultrasonic energy having a frequency of 0.8 mega-cycles per second at an intensity of 20 watt/cm². The vibrator was located in the centre of the lower end of the tubular reactor. 88.1 kg. of precipitated calcium carbonate having a purity of 98.95% by weight and an apparent density of 177 g/litre were obtained.

WHAT WE CLAIM IS:—

1. A process for the production of substantially pure powdered calcium carbonate and/or a solution of magnesium bicarbonate from a natural mineral containing calcium or magnesium carbonate, or both, which comprises calcining the natural mineral to convert its carbonate to oxide, slaking the oxide(s) with water to give hydroxide(s), reacting the resulting suspension of the hydroxide(s) with carbon dioxide in a reactor in which said hydroxide suspension and gases comprising carbon dioxide are introduced at substantially the same pressure and are forced to flow continuously upwardly under pressure against gravity, and thereafter recovering the powdered calcium carbonate and/or solution of magnesium bicarbonate.
2. A process as claimed in claim 1 wherein the hydroxide suspension is vibrated during the reaction with carbon dioxide.
3. A process as claimed in claim 2 wherein the vibration is ultrasonic vibration.
4. A process as claimed in any one of the preceding claims in which calcium carbonate is recovered by filtration under pressure.
5. A process as claimed in any one of the preceding claims wherein the carbon dioxide is passed into a reactor through a porous or perforated surface.
6. A process as claimed in any one of the preceding claims wherein the carbon dioxide employed is derived from the calcination step or from the solution of magnesium bicarbonate.
7. A process as claimed in any one of the preceding claims wherein the reactor employed has a tubular reaction space, the longitudinal axis of said reaction space deviating not more than 15° from the vertical, the average cross-sectional area of said reaction space being not more than 1200 cm² and the length of said reaction space being at least 15 times its average diameter.
8. A process as claimed in claim 7 wherein there is a vibrator adjacent the reactor for vibrating the reactants during the carbonation reaction.
9. A process as claimed in claim 8 wherein the vibrator is an ultrasonic vibrator.
10. A process as claimed in claim 1 substantially as herein described.
11. A process as claimed in claim 1 sub-

stantially as herein described with reference to the foregoing Examples.

12. Powdered calcium carbonate whenever prepared by a process as claimed in any one of the preceding claims.

5 13. A solution of magnesium bicarbonate wherever prepared by a process as claimed in any one of claims 1 to 3 or 5 to 11.

14. Magnesium carbonate or oxide wherever prepared from magnesium bicarbonate 10 as claimed in claim 13.

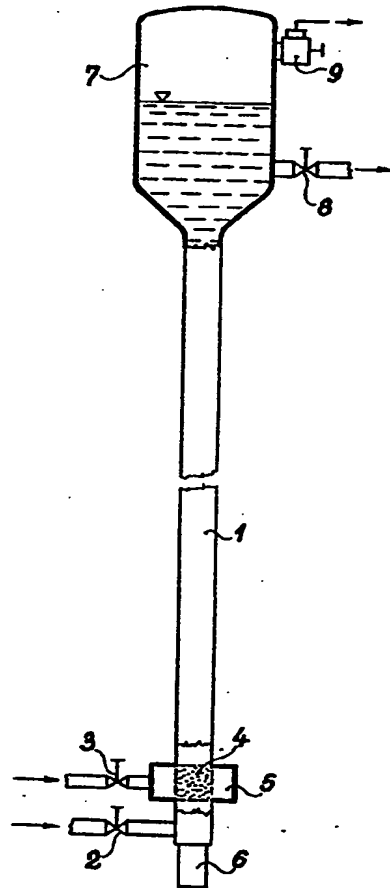
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1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*



Improvements in or relating to the production of calcium and magnesium carbonates

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Abstract

Powdered calcium carbonate and/or a solution of magnesium bicarbonate are prepared from a natural mineral containing calcium or magnesium carbonate or both, by heating the mineral to convert the carbonate to oxide, slaking the oxide with water to give hydroxide, reacting the resulting solution or suspension of hydroxide with carbon dioxide in a reactor in which both the hydroxide solution or suspension and the carbon dioxide are forced to flow continuously upwardly under pressure against gravity, and thereafter recovering the powdered calcium carbonate and/or solution of magnesium bicarbonate. The hydroxide solution or suspension may be subjected to vibration, preferably ultrasonic vibration, during the reaction with carbon dioxide as may the oxide during slaking. The carbon dioxide may be derived from the calcination of a naturally occurring carbonate mineral and may be introduced into the reactor through a porous or perforated surface to distribute it in the form of fine bubbles. The calcium carbonate may be recovered by filtration under pressure. The reactor may comprise a tubular reaction space, the longitudinal axis of which does not deviate by more than 15 degrees from the vertical, the average cross-sectional area of which is not more than 1200 cm.² and the length of which is at least 15 times its average diameter. It may be fitted with a vibrator preferably an ultrasonic vibrator, for vibrating the reactants during the carbonation reaction. The solution of magnesium bicarbonate obtained may be used to prepare magnesium oxide which may be employed to prepare magnesium metal by chlorination and electrolysis of the magnesium chloride so obtained, pure carbon dioxide being a useful by-product.

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